SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF A PROVINCIAL WATER QUALITY OBJECTIVE FOR COBALT (STABLE ISOTOPE)

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A PROVINCIAL WATER QUALITY OBJECTIVE

FOR COBALT

(STABLE ISOTOPE)

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PREFACE

The Ontario Ministry of Environment and Energy develops Provincial Water Quality Objectives, or Interim Objectives, for those substances deemed to be of greatest environmental concern in Ontario. These as determined through a screening process which considers persistence, potential to bioaccumulate, acute and chronic toxicity and potential presence in the aquatic environment. Alternatively, Ministry staff who have a direct responsibility for managing possible effects of these chemicals may request an evaluation.

Provincial Water Quality Objectives and Interim Objectives (PWQO/IOs) are numeric or narrative criteria intended to protect all life stages of aquatic organisms for indefinite exposures and/or to protect recreational uses of water. PWQO/IOs for recreational uses, including swimming, are currently based on microbiological and aesthetic considerations. The potential for harmful effects from exposure to chemical substances during recreational uses is unknown at present, but will be considered when scientific information becomes available. Ontario Drinking Water Objectives and sport fish consumption guidelines are also considered in protection of human health. PWQO/IOs represent a desirable water quality for the protection of designated uses of surface waters in Ontario. PWQO/IOs do not take into account analytical detection or quantification limits, treatability or removal potential, socio-economic factors, natural background concentrations, or potential transport of contaminants among air, water and soil. These factors are considered in policies and procedures which govern the uses of PWQO/IOs, contained in the booklet, Water Management: Policies, Guidelines and Provincial Water Quality Objectives of the Ministry of Environment and Energy (OMOEE 1994a), which deals with all aspects of Ontario's water management policy.

The process for deriving these criteria is detailed in Ontario's Water Quality Objective Development Process (OMOE 1992a). The toxicology literature is reviewed for all of the following areas: aquatic toxicity, bioaccumulation, mutagenicity, and aesthetic considerations. The final Objective/Interim Objective is based on the lowest effect

concentration reported for any of these factors on aquatic organisms as well as taste and odour considerations of the water. Where there are reliable and adequate data, an Objective is developed using a safety factor. Where there are fewer data, an Interim Objective is developed using an "uncertainty factor". The size of the uncertainty factor reflects the availability of appropriate data and the potential of the material to bioaccumulate. Interim Objectives can be promoted to Objectives when sufficient reliable data become available.

PWQO/IOs are used to designate surface waters of the Province which should not be further degraded. They are also used in receiving water discharge assessments and may be included in Certificates of Approval which are issued to regulate effluent discharges. Where better water quality is required to protect other beneficial uses of the environment in a given location, appropriate criteria and factors, including public health considerations, are taken into account.

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SUMMARY

A Provincial Water Quality Objective (PWQO) was developed for cobalt for the protection of aquatic life. Available information on the physical-chemical properties, aquatic toxicity, bioaccumulation potential, taste and odour characteristics and genotoxicity potential of cobalt were considered in developing the Objective.

Cobalt is an element which occurs naturally in the earth's crust. Approximately 10% of the world's total production of cobalt comes from Canada. Cobalt is used in various alloys, as a catalyzing agent, fertilizer and as a colouring agent in glass and ceramics. It is also used in the medical field and as a farm feed additive.

Cobalt is found in trace amounts in surface waters of Ontario. In the Great Lakes, total cobalt concentrations rarely exceed the detection limit of 1 µg/L, however concentrations as high as 80 µg/L have been reported in surface water near mine tailings.

Cobalt exists in surface waters mainly as the divalent and trivalent forms. Cobalt is strongly adsorbed on suspended solids and sediments, Therefore very low concentrations are found in the dissolved state. In most ecosystems, the sediment is the primary sink for cobalt.

Compared to other metals, cobalt is slightly to moderately toxic. The literature indicates that acute effects for a variety of aquatic life occur between 1 mg/L and 450 mg/L. Chronic effects range from 0.009 mg/L to 2 500 mg/L. Cobalt does not appear to bioaccumulate to any significant degree in fish.

There was sufficient aquatic toxicity data available to derive a Provincial Water Quality Objective. **The recommended PWQO for cobalt is 0.0009 mg/L (0.9 µg/L) derived by dividing the lowest acceptable effect concentration of 0.009 mg/L (28d reproduction impairment and reduced survival of *Daphnia magna*) by an safety factor of 10.**

The PWQO is above the OMOEE laboratory detection limit, however due to difficulties in analysis, often the detection limit may be higher than the PWQO. This value should be protective of effects due to aquatic toxicity, bioaccumulation, taste and odour effects. There are indications that exposure to cobalt may cause mutagenicity. However insufficient information was available to assess these effects on aquatic organisms.

Note: Concentrations in this document are expressed in a number of different units commonly used in scientific papers. The conversion factors are:

1 gram per litre (g/L) = 1000 milligrams per litre (mg/L)
1 milligram per litre (mg/L) = 1000 micrograms per litre (µg/L)

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1.0 INTRODUCTION

Cobalt (Co) is a silver-grey, hard, magnetic, ductile, and somewhat malleable metal similar to nickel and iron in appearance (Sax and Lewis 1989; Weast *et al.* 1987; Windholz *et al.* 1983). It is the 30th most abundant element on earth and comprises approximately 0.0025% of the earth's crust (Kirk *et al.* 1979). ASTDR (1991) reports tnat cobalt frequently occurs in nature in association with nickel, and often with arsenic. In Cobalt, Ontario, deposits of cobalt occur with silver (Hawley, Pers. comm). Cobalt is found in various rock types present in Ontario, namely granite, basalt, shale, limestone, and sandstone. Common ores may contain the minerals cobaltite ($CoS_2.CoAs_2$), linnaeite (Co_3S_4), carrollite, safflorite, skutterudite, smaltite ($CoAs_2$), and erythrite ($3CoO.As_2O_5.8H_2O$) (Shamberger 1979; Windholz *et al.* 1983). The average total cobalt concentration in Ontario soils is 4.4 mg/kg (Young 1979), while that in tailings deposits is 83 mg/kg (Hawley, 1980).

Cobalt is an essential nutrient required for vitamin B_{12} metabolism. In mammals, Co deficiency and low levels of vitamin B_{12} result in pernicious anemia, whereas excess results in polycythemia (Martell 1975).

1.1 PRODUCTION AND USES

Cobalt was used as a colouring agent as far back as 2000 BC by the Egyptians, and later by the Assyrians, Greeks, Romans, and Chinese (Kirk *et al.* 1979). By the 17th century, Europeans had discovered methods of mining cobalt and used it to colour glass and pottery. In 1914, the first cobalt produced commercially in the world was manufactured at Deloro, Ontario. The plant at Deloro was closed down in 1961 due to the slumping demand for cobalt (Azcue and Nriagu 1993). Today there are numerous uses for cobalt, including uses in the industrial, agricultural and medical sectors.

Important cobalt deposits occur in Zaire, Morocco, Australia, and Canada (Weast *et al.* 1987). The reserves of Canada and Australia comprise about one quarter of the world

supply (Kirk *et al.* 1979). Emsley (1991) reports that 1984 world production of cobalt was 19 000 tonnes. In Canada, cobalt is produced mainly in Ontario and Manitoba (CCREM 1987) as a by-product of nickel-copper production.

Giancola (1994) reports that in 1993 there were nine mines in Ontario which produce cobalt. All were in the Sudbury area. Cobalt is only incidently mined from these deposits, primary ores are nickel, silver and copper (Hawley, Pers. comm). In 1993 the cobalt content of metal concentrates produced in Canada was 2 370 tonnes, of which approximately 2 000 tonnes were produced in Ontario (NRC 1994, OMNDM 1994). Ontario ranked fourth in world cobalt production, accounting for 11% of the world total (OMNDM 1994). Zambia was the world's largest producer in 1993 accounting for 25% of total production.

Cobalt is used in various alloys including super-alloys, magnetic alloys (for the manufacturing of jet and gas turbines, and stainless steels), dental and surgical alloys (CCREM 1987; Shamberger 1979). Cobalt and its salts are also used in cemented tungsten carbides, glass and ceramic paints, hygrometers, as catalysts for organic reactions, in electroplating, fertilizers, and as a foam stabilizer in beer (Shamberger 1979; Sittig 1985; Windholz *et al.* 1983). Therapeutically, cobalt or cobalamin (vitamin B12) is used in the treatment of cyanide poisoning and as a feed additive to correct deficiency symptoms such as anaemia and retarded growth (Beliles 1979).

Radioactive cobalt-60 is used as an anti-neoplastic gamma ray source. However cobalt-59 has been found to be a possible (experimental) neoplastigen and tumorigen (Sax and Lewis 1989; Sittig 1985; Windholz *et al.* 1983). Radioactive properties of cobalt will not be further addressed.

1.2 AQUATIC SOURCES AND FATE

Cobalt residence time in the atmosphere is quite short. It is more likely to be found in sediments, soils and water. It is estimated that weathering of rock and soils contributes

between 17 and 20% of the natural global emissions for cobalt, whereas biological action by plants contributes 60% (Merian 1984).

Coal contains on average about 1 mg/kg cobalt, but concentrations can range up to 40 mg/kg. Combustion of coal is a major anthropogenic source of cobalt to the environment (Merian 1984). Other anthropogenic sources include acid coal mine drainage, smelter emissions, raw and treated sewage (0.002-0.04 mg/kg and 0.001 and 0.03 mg/kg, respectively), and application and losses of cobaltous sulphate-containing fertilizers (Smith and Carson 1981).

Recent effluent discharge data are available from Ontario's Municipal/Industrial Strategy for Abatement (MISA) monitoring reports. Ten sectors (iron and steel, organic chemical manufacturing, pulp and paper, metal mining, metal casting, industrial minerals, inorganic chemicals, petroleum, waste water treatment plants and hydro-electric generation) were required to monitor effluent quality for a one year period (OMOE 1988, 1990, 1991a-f, 1992b, 1993). Quantification of the total mass (effluent flow X effluent concentration) of cobalt discharged to Ontario's surface waters could not be determined reliably because many of the data were at or below the regulatory method detection limit (20 µg/L). The data suggest that these industries contribute approximately 36 kg of cobalt per day to Ontario watersheds. However, intake data suggest that 50-90% of cobalt in the discharge was merely entrained by the industry. Significant dischargers of cobalt are the Mining Sector and the Municipal Sewage Treatment plants, each contributing approximately 1/3 of the total discharge. However, recent closures of uranium mines in Ontario have reduced mining sector discharge of cobalt by about 25% (Hawley, Pers. comm).

1.3 AMBIENT CONCENTRATIONS IN ONTARIO WATERS

Boomer (pers. comm.) reports that the routine OMOEE laboratory detection limit for cobalt in surface water is currently 0.5 µg/L using pre-concentrated samples and ICP/MS technology. However, there are problems when using this technique with samples containing high concentrations of iron. Iron emits photons at a wavelength similar to that

of cobalt, resulting in interference. This may result in a detection limit 2-3 orders of magnitude higher for samples containing high concentrations of iron. In general, OMOEE data such as the Provincial Water Quality Monitoring Network (PWQMN) data or the Great Lakes Surveillance Data report a detection limit of 1 µg/L. The MISA Regulatory Detection Limit (RMDL) for cobalt was 20 µg/L.

Cobalt concentrations in oxygenated surface waters in Canada range from 1 to 47 µg/L (NAQUADAT 1985, as cited in CCREM 1987) and are generally below 20 mg/kg in freshwater sediments (Smith and Carson 1981). Background concentrations of cobalt were higher in Lake Erie water than in Lake Ontario water, and were the lowest in Lake Superior waters. Median values of dissolved, particulate, and total cobalt were 0.089, 0.005, and 0.096 µg/L, respectively, for Lake Erie; and 0.021, 0.0037, and 0.025 µg/L, respectively for Lake Ontario (Rossmann and Barres 1988).

Monitoring data from the Ontario Ministry of Environment and Energy (OMOEE 1994b) suggest that cobalt concentrations are generally below the detection limit of 1 µg/L in the Great Lakes. For some areas, in particular the St. Clair River, concentrations as high as 10 µg/L have been reported, but it is unknown whether this is due to natural or anthropogenic sources. While effluent data collected under the MISA program from organic chemical manufacturing industries along the St. Lawrence River suggest that cobalt may be being discharged, OMOEE data (OMOEE 1994b) report all values were below 1 µg/L at seven ambient stations along the river.

Data were also available for Ontario inland waters collected under the Provincial Water Quality Monitoring Network (OMOEE 1994c). Most areas monitored had cobalt concentrations below the detection limit (1 µg/L), however there are areas that are significantly contaminated with cobalt. These areas are generally downstream of mining sites, particularly abandoned uranium mines. Waterbodies around Bancroft (NE Ontario), including Farrell Creek, Paudash Lake, Deer Creek and Centre Lake contain cobalt concentrations of 30 to 50 µg/L. Surface water around Cobalt, Ontario contain similar concentrations of cobalt. The Trent River, near Peterborough, had concentrations of 30-40

µg/L cobalt, although there are no mines in the area. Tailings ponds and waterbodies downstream of Bicroft Mine (also in the Bancroft area) contained concentrations ranging from 25 to 60 µg/L, while areas around Balmer Creek (NW Ontario near Red Lake) had concentrations as high as 80 µg/L.

The Bicroft mine, and many of the others in the Bancroft area have been abandoned for more than 20 years (Hawley, pers. comm.). However PWQMN data suggests that leaching from the tailings is still of concern. It should be noted that the highest concentrations were found directly in tailings ponds, and waterborne concentrations of cobalt decreased steadily downstream due to dilution and/or sorption to sediments.

Ambient cobalt concentrations in the suspended solids of the Niagara River and the sediments of Lake Ontario (Niagara Basin) were 0.021 and 0.017 mg/kg, respectively (Thomas 1983).

Deloro, in southwestern Ontario (about 60 km NE of Peterborough) is the site of an abandoned gold mining and refining site, which has a long history of metal contamination (Azcue and Nriagu 1993). Cobalt, mined in Cobalt, ON or imported from outside the province, was brought to the site for refining. Tailings contained high concentrations of cobalt which leach into the Moira River. Although the refinery was closed in the 1960's, and a tailings treatment plant has been built on-site, elevated concentrations of cobalt are still detected in the Moira River. Just downstream of the Deloro site, levels of cobalt ranging from 1 to 20 µg/L were detected. Cobalt concentrations in samples collected further downstream ranged from 1 to 10 µg/L, while at the mouth of the river (near Belleville) levels were below the detection limit (OMOEE 1994c). Mudroch and Capobianco (1979) correlated cobalt concentrations in surface sediments to those in submerged macrophytes of the Moira River drainage basin. For samples collected at the same site, cobalt concentrations in surface sediments and in the macrophytes *Myriophyllum verticillatum* and *Elodea canadensis* were 864, 262.5 and 10 µg/g dry weight, respectively (Mudroch and Capobianco 1979).

1.4 AQUATIC CHEMISTRY

Cobalt metal (molecular weight 58.9) has a melting point of 1 493 °C and a boiling point of 3 100 °C, and is stable in air and water at standard temperatures (Sax and Lewis 1989; Windholz *et al.* 1983). There are six oxidation states for cobalt -1, 0, +1, +2, +3, and +4 In general the common valence of cobalt is +2 (cobaltous ion), except in coordination complexes where the +3 (cobaltic ion) predominates (Shamberger 1979).

In aqueous solution the cobaltous ion (Co II) is stable but the uncomplexed cobaltic ion (Co III) is a strong oxidizing agent (Trisdan *et al.* 1981). Based on simulations using the MINEQL-1 model, cobalt metal should exist mainly as aquo ions (i.e. as an ion containing water molecules) over a pH range of 4 to 7 (Campbell *et al.* 1982; Campbell and Stokes 1985).

ASTDR (1991) reports that in most freshwaters, less than 2% of cobalt species are present in the dissolved state, most cobalt is precipitated or adsorbed on suspended solids or sediments. However, the data from Rossmann and Barres (1988) Lakes Erie and Ontario does not indicate the same ratio, with cobalt existing almost entirely in the dissolved state in Lake Erie and existing in about equal proportions in Lake Ontario. Nriagu and Coker (1980) determined that only 2-5% of cobalt was associated with humic acids in Lake Ontario sediments. Illite clay suspensions (1 g/L), adsorbed 95% of cobalt at pH 8 and 40% at pH 4 at concentrations from 50 to 200 µg/L (O'Connor and Kester 1975 as cited in CCREM 1987). Adsorption of cobalt to clay minerals was found to increase with increasing pH (Carson 1981; Murray and Murray 1973). In most waters, the sediment is the primary repository site of cobalt. Some mobilization may occur in acidic waters, in the presence of excess chloride ions or chelating agents. Chelation of cobalt with ligands such as EDTA, increases its solubility and mobility in the aquatic environment (CCREM 1987).

2.0 TOXICITY TO AQUATIC ORGANISMS

All candidate toxicological information is screened for acceptability. All information that meets the following requirements is considered primary data:

- Toxicity tests must employ accepted laboratory practices of exposure and environmental controls. While all tests must be evaluated on a case by case basis, those tests following published protocols of government agencies or standard setting associations are generally acceptable.

- Any tests may be acceptable, including static tests if it can be shown that concentrations of the toxicant are not changing (significantly) throughout the test and adequate environmental conditions for the test species are maintained with respect to such factors as dissolved oxygen and removal of metabolic wastes. Generally, continuous flow exposures, and renewal tests (i.e. static tests with replacement) are acceptable if appropriate rates of renewal of toxicant are maintained. Static tests are acceptable if concentrations of the toxicant are measured in the exposure vessel at the beginning and end of the test and no more than 10% of the toxicant is lost during the test. The use of chemical carriers is acceptable as long as the concentration of the toxicant does not exceed water solubility in the absence of the carrier. Appropriate chemical carrier controls must also be included.

- Dissolved concentrations of toxicant in the exposure vessels must be constant and verified by measurements rather than calculated or measured only in stock solutions. Tests will generally be considered unacceptable if more than 10% of the toxicant is lost during the test.

- Test end points and lengths of exposure must be appropriate to the life stage of the species tested and the characteristics of the substance. Although the definitive bench mark for chronic toxicity is a whole life cycle test, partial life cycle and short term or early life stage tests are acceptable as chronic data.

- Relevant environmental parameters such as temperature, pH and hardness must have been recorded

- Responses and survival of controls must be appropriate for the species and test used.

Data on vertebrates and invertebrates not meeting all of the above are denoted as secondary in objective development documents. Secondary data are inadmissible in the derivation of an Objective but are admissible in deriving an Interim Objective. Most tests using aquatic plants will also be classified as secondary due to the frequent use of artificial media or a lack of standardized protocols; however, plant data may be used as the critical endpoint for Objective development subject to best scientific judgement.

Toxicity data, current to February 1995, are summarized in Table 2. These data were critically reviewed and classified as primary, secondary or ancillary data based on the laboratory practices of the researchers. A more detailed explanation of the classification procedure is outlined in "Ontario's Objective Development Process" (OMOE 1992a).

2.1 ACUTE TOXICITY

2.1.1 Vertebrates

There were two primary studies with vertebrates, both using fathead minnows (*Pimephales promelas*). Additionally, there were four secondary studies on two fish species and one frog species.

Diamond *et al.* (1992) reported hardness-dependent 48h-NOECs (No Observable Effect Concentrations) for fathead minnows of 1.2, 7.3, 13.7 and 6.2 mg/L for hardnesses of 50, 200, 400 and 800 mg/l $CaCO_3$, respectively. These tests were done under static conditions with daily renewals. The authors reported that LC50 values for fathead minnow tests could not be calculated due to the unexpectedly low sensitivity of this species to high cobalt concentrations ($\geq$ 5 mg/L) over the 48h exposure period. Kimball (undated MS),

however, reported a 96h-LC50 of 3.61 mg/L, also using fathead minnows. These tests were done under flow-through conditions with a 5.8h turn-over time. It is unknown why Kimball (undated MS) was able to derive a result with concentrations less than 5 mg/L, while Diamond *et al.* (1992) was not. The longer exposure time may be the main reason, since Kimball (undated MS) also reported a 192h-LC50 of 2.74 mg/L under the same conditions, suggesting exposure periods have a significant effect on toxicity. These data were considered primary as they employed good laboratory practices using measured toxicant concentrations.

Secondary acute toxicity data were available for giant gouramis (*Colisa fasciatus*), fathead minnows, and african clawed frogs (*Xenopus laevis*). 96h-LC50 values ranged from 22 to 13 500 mg/L (Srivastava and Agrawal 1979; Ewell *et al.* 1986; Curtis and Ward 1981; Sunderman 1992). Frogs exposed to a cobalt concentration of 5.453 mg/L exhibited decreased growth and an exposure to a concentration of 0.325 mg/L resulted in 50% embryo abnormalities after 96h, suggesting that sub-lethal effects may result at lower concentrations than those needed for lethal effects (Sunderman 1992). The original paper for this study could not be obtained, thus it was ranked as secondary.

Srivastava and Agrawal (1979) reported a 96-h LC50 of 225 mg/L of cobalt chloride for the freshwater teleost, *Colisa fasciatus*. Although the LC50 was based on the salt, they did not state whether it was anhydrous or hexahydrate. The conversions of the LC50, assuming the salt used to be anhydrous or hexahydrate, results in 96h-LC50 values of 102.1 mg Co^{2+}/L or 55.7 mg Co^{2+}/L respectively. In addition to the 96-h LC50, Srivastava and Agrawal (1979) reported that a 90-h exposure of the fish to a sublethal concentration of 195 mg/L cobalt chloride salt caused a decrease in blood clotting time, an increase in circulating thrombocytes, and leucopenia.

2.1.2 Invertebrates

There were three primary studies with three species of freshwater invertebrates (two crayfish species and one daphnid). Secondary data were available for eleven species.

Most data were EC50s with exposure times varying from 24 to 96h. Acute toxicity values ranged from about 1 mg/L to 500 mg/L. Daphnids appear the most sensitive invertebrate to cobalt, while *Tubifex* appear to be the most tolerant.

Biesinger and Christensen (1972) reported 48-h EC50 values for *Daphnia magna* of 1.62 mg/L and 1.11 mg/L, with and without food, respectively. It appears that either the toxicity of cobaltous chloride hexahydrate was reduced in the presence of added food, or toxicity was enhanced in unfed organisms due to the stress of starvation. Khangarot *et al.* (1987) reported two 24-h EC50s and two 48-h EC50s by applying different statistical methods to the same raw data for *Daphnia magna*. The 24-h EC50s were 2.11 mg/L and 2.61 mg/L with cobaltous chloride hexahydrate as the toxicant. The 48-h EC50s were 1.52 mg/L and 1.49 mg/L (Khangarot *et al.* 1987). Baudouin and Scoppa (1974) reported a 48-h EC50 value of 1.32 mg/L for *D. hyalina* using hexahydrated cobaltous chloride salt as the toxicant.

Kimball (undated MS) conducted replicated acute tests with *D. magna*. Tests used neonates <24-h old and were static, lasting either 48 h with and without feeding, or 96 h only if fed. This experiment involved measured toxicant conditions and was considered primary. Feeding decreased the toxicity of cobalt at 48h. The 48h-EC50s of cobalt were 7.37 and 5.99 mg/L for daphnids that were fed and not fed, respectively. It is not clear however if the effect was due to increased stamina of the *Daphnia* or interference with the toxic action.

Diamond *et al.* (1992) reported 48h-EC50s for *D. magna* at four water hardness levels. Reported values were 2.3, 4.6, 4.2 and >5.3 mg/L at hardness values of approximately 55, 255, 475, and 880 mg/L as $CaCO_3$, respectively. This experiment was considered primary. The data suggests that toxicity is inversely proportional to water hardness.

Boutet and Chaisemartin (1973) reported 96h-LC50s of 8.8 mg/L and 10.2 mg/L, for two species of crayfish, *Austropotamobius pallipes pallipes* and *Orconectes limosus*, respectively. Both of these studies used measured toxicant concentrations and were

considered primary. In most cases, invertebrate studies lasting more than 48h are considered chronic. However, crayfish life cycles tend to be longer in duration and a single life stage may last for longer than 96h. Thus, these 96h experiments were considered to be acute.

2.2 CHRONIC TOXICITY

2.2.1 Vertebrates

Three primary chronic studies using four species of vertebrates were found (Birge 1978, Kimball undated MS, Diamond *et al.* 1992). In addition, two studies were classified as secondary. Toxicity values for cobalt ranged from 0.05 mg/L for a 7d-LC50 for the narrowmouth toad (*Gastrophryne carolinensis*) to 15 mg/L resulting in haematological changes in tilapia (*Sarotheradon mossambicus*).

Birge (1978) obtained a 28-d LC50 of 0.47 mg/L for rainbow trout embryos. For goldfish (*Carassius auratus*) and the narrow mouthed toad, the 7-d LC50 values were 0.81 mg/L and 0.05 mg/L, respectively (Birge 1978).

Chronic toxicity of cobalt to fathead minnows was tested by Kimball (undated MS) starting with eggs <40-h old and lasting until 28 days post hatch. At 1.61 mg/L there was a small decrease in hatch success, however all fry were reported to have developmental abnormalities. Only 23% of fathead minnows survived for 28d at 1.61 mg/L. Weight gain was a more sensitive endpoint however, and fish exposed to 0.81 mg/L gained significantly less weight than controls. Kimball (undated MS) reported that cobalt ranked fourth of seven metals tested on fathead minnows for growth inhibition.

Jones (1939a) reported a 10-d NOEC of 10 mg/L for the stickleback *Gasterosteus aculeatus* with cobaltous nitrate as the toxicant. The author observed that cobaltous nitrate and several other salts of metals such as silver, precipitated with the mucus secreted by the fish. Noticing an increase in the frequency and amplitude of respiratory movements, Jones (1939a) postulated that this compensatory reaction was not adequate

to overcome impairment of respiratory function due to the physical clogging of the gill filaments by the precipitates, thus resulting in death by asphyxiation.

Diamond *et al.* (1992) examined the effects of hardness on survival and growth of fathead minnows over seven days. While the data suggest that increasing hardness may decrease chronic cobalt toxicity, the authors felt that there were too few chronic data available to determine a definite relationship between cobalt toxicity and water hardness.

2.2.2 Invertebrates

Four primary chronic studies with three species of invertebrates were found. An additional twelve secondary chronic studies were also identified. Toxicity values of cobalt ranged from a low of 0.00016 mg/L causing terata in snail embryos to 139.32 mg/L for a 96h-LC50 for tubificids. Chronic studies investigate many types of toxic effects, both lethal and sublethal, over a wide range of exposure times and it is not surprising that there is such a large range of toxicity values.

Diamond *et al.* (1992) examined the effects of hardness on *D. magna* using 7-d survival and reproduction experiments. The authors reported that a number of experimental problems caused difficulty in analyzing the results, and they reported that NOECs could only be calculated for one hardness level (400 mg/L as $CaCO_3$) which was reported as <50 µg/L. The authors do report, however, that their experiments suggest a hardness dependant relationship for cobalt toxicity.

Boutet and Chaisemartin (1973) determined the 30-d LC50 for two species of crayfish, with and without food. For *A. pallipes pallipes* the 30-d LC50 was 0.77 mg/L with food, and 0.79 mg/L without food. Similarly, the 30-d LC50 for *O. limosus* was 0.79 mg/L with food, and 0.88 mg/L without. Thus, the addition of food had little effect on the toxicity of cobalt as cobaltous chloride hexahydrate.

Biesinger and Christensen (1972) exposed *D. magna* to cobalt chloride hexahydrate for 3 weeks and reported the LC50 and sublethal effects. The 21-d LC50 was 0.021 mg/L, while a concentration of 0.024 mg/L caused a 15% reduction in weight as well as 12% and 45% increases in protein and glutamic oxalacetic transaminase (GOT), respectively. These physiological responses occurred at Co^{2+} levels greater than the LC50. Reproduction was impaired by 16% and 50% at cobalt concentrations of 0.010 mg/L and 0.012 mg/L, respectively (Biesinger and Christensen 1972). Kaiser (1980) was able to accurately predict the 16% reproductive impairment concentration given by Biesinger and Christensen (1972), using an equation that incorporated ion-specific physical-chemical properties (*e.g.*, ionization potential and oxidation state).

Chronic toxicity of cobalt to *D. magna* was tested by Kimball (undated MS). Tests were static with replacement and measured survival and several indices of reproductive success. The 28-d LC50 was 0.027 mg/L Co, almost identical to that of Biesinger and Christensen (1972). Kimball (undated MS) reported that tests using *Daphnia* reproduction as the endpoint were much more sensitive than those using lethality. The lowest concentration of cobalt which significantly decreased reproduction (as mean young per female) was 0.009 mg/L. Kimball (undated MS) also compared the sensitivity of *Daphnia* and fathead minnows to nine metals (V, Se, Tl, Co, Sb, Mn, Al, Mo and Be). For most metals, the toxicity was similar for both organisms although the order of sensitivity changed somewhat. In the case of cobalt however, *Daphnia* were nearly 60 times more sensitive than fathead minnow. Compared to the toxicity of other metals, cobalt ranked fifth of the nine metals tested on daphnids.

Sodergren (1976) reported a 96-h LC50 of 33 mg/L for the nymph of damselflies (*Ephemerella mucronata*) exposed to cobalt nitrate. Cobalt toxicity was tested on *E. ignita* nymphs in the presence of a food source *Fontinalis dalecarlica.* A four week exposure to 0.0326 mg/L of cobalt nitrate resulted in reduced growth (Sodergren 1976). A possible explanation for the higher toxicity to *E. ignita*, presented by Sodergren (1976), is that the nymphs received a greater dose of cobalt by consuming *F. dalecarlica*, which accumulates

cobalt. However, the observed toxicity may simply be a function of the longer exposure period. These data were considered secondary.

A solution of cobaltous chloride at 10 mg/L of Co^{2+}, was found to completely inhibit nuclear expansion in the chloragocytes of *Tubifex tubifex* under hypoxic conditions (Fischer *et al.* 1980). Under aerobic conditions cobalt had neither a stimulatory nor an inhibitory effect on nuclear expansion. The authors surmise that since cobalt is an effective inhibitor of haem synthesis and possibly an inhibitor of globin synthesis, the depression of nuclear expansion may be the result of cobalt's inhibitory effect on haemoprotein synthesis.

The probit-derived 96-h EC50 estimate for the rotifer, *Philodina acuticornis*, exposed to cobalt chloride was 27.8 mg/L with an endpoint criterion of no visible internal or external motion (Buikema *et al.* 1974). Hardness of the water had little effect on cobalt toxicity in this study.

Solski and Piontek (1987, in AQUIRE) reports planaria exposed to 0.002 to 0.028 mg/L cobalt for 10 days showed a change in the ability to regenerate. This paper could not be obtained and critically reviewed, and thus could not be used for criteria development.

Based on 96h-EC50 studies with *T. tubifex*, Khangarot (1991) found that cobalt ranked 24th of 32 elements tested. Cobalt was found to be twice as toxic to *Tubifex* than magnesium, calcium and sodium, but at concentrations significantly less toxic than metals such as lead, mercury or cadmium.

2.2.3 Other Organisms (Algae, Protists etc.)

According to the Objective Development Process (OMOE 1992a), tests employing algae are always classified as secondary data due to inherent difficulties in performing algal experiments.

Toxicity studies were available for seven species of algae and two protists. Toxicity values ranged from 0.1 mg/L to 50 mg/L for algae, while 3h-HTC (highest concentration where protists were still observed alive after three hours) ranged from 1 000 to 2 500 mg/L.

Cobalt toxicity to algae was in the same order of magnitude as that of copper and nickel (den Dooren de Jong 1965). For *Chlorella vulgaris*, the growth inhibition NOEC and LOEC (lowest observed effect concentration) values were 0.226 mg/L and 0.442 mg/L Co^{2+} as cobalt chloride hexahydrate, respectively (den Dooren de Jong 1965). Hutchinson (1973) reported 99% growth inhibition of this same species at 1.0 mg/L. For the more tolerant species *Haematococcus capensis*, growth was inhibited by 80% at 5.0 mg/L (Hutchinson 1973). A more sensitive species was *Chlamydomonas eugametos*, which had 100% growth inhibition at 0.5 mg/L (Hutchinson 1973). Other toxicity tests with algae showed that concentrations of cobalt chloride between 2 and 9 mg/L Co^{2+} were toxic to *Anabaena variabilis*, whereas, concentrations between 20 and 50 mg/L were toxic to *C. vulgaris* (Ahluwalia and Kaur 1988). Stokes (1981) reported EC50 values of 0.25 mg/L for *Scenedesmus acutiformis f. alternans* and 0.1 mg/L for *S. acuminatus*. Sharma *et al.* (1987) found *Spirulina platensis* to be less sensitive to cobalt than other algae, with a 96-h EC50 of 23.8 mg/L. The endpoint criterion in this study was dry weight biomass as a function of optical density at 490 nm and sublethal concentrations (0.1 and 0.5 mg/L) resulted in an increase in biomass, which was ascribed to a hormetic effect.

2.3 SUMMARY OF TOXICITY DATA

Insufficient data prohibits comparison of the relative toxicities of the various forms of cobalt to aquatic biota.

In general, acutely toxic concentrations from primary references indicated effects in the 1 to 10 mg/L range, except when organisms are exposed in very hard water, while secondary values were as high as 450 mg/L. Toxicity values fall within the same range for both vertebrates and invertebrates, however there are too few acute vertebrate studies for accurate comparison. Chronic toxic concentrations of cobalt from primary references

suggest that effects are likely to occur in the range of 0.009 to 2 mg/L, while secondary studies ranged from 0.0016 to 2 500 mg/L. In general, chronic data tend to vary more widely than acute data due to the wide range of exposure times and types of endpoints examined. Primary data suggest that invertebrates may be more sensitive to cobalt than vertebrates under chronic exposures. Kimball (undated MS) reported that *Daphnia* are more sensitive to cobalt than fathead minnows when exposed for 96h, however the extent of the difference is not very large. Data comparing growth of fathead embryos and *Daphnia* survival and reproduction suggested that *Daphnia* were approximately 60 times more sensitive to cobalt than are fathead minnows (Kimball undated MS).

Khangarot and Ray (1989) summarized how cobalt toxicity compared to the toxicity of other metals tested on various aquatic species (Table 1). Cobalt tends to be slightly to moderately toxic, however some species appear to be especially sensitive. Kimball (undated MS) found that *Daphnia magna* were more sensitive to cobalt than many other minor inorganics (*e.g.*, beryllium, selenium, thallium *etc.*). However, this study did not expose organisms to metals such as mercury, cadmium or lead, that other experiments have shown to be much more toxic. For example, Khangarot and Ray (1989) found that cobalt was approximately 1000 times less toxic than mercury. Birge (1978) ranked cobalt in an arbitrarily determined, Toxicity Group 1, based on toxicity studies with toads, goldfish and rainbow trout. This category included more toxic metals such as silver, mercury, and cadmium.

Table 1: Toxicity ranking of cobalt compared to other metals (modified from Khangarot and Ray 1989)

Species Tested	Endpoint	Cobalt Ranking	# of Metals Tested	Reference
Chlorella vulgaris	EC50	8	9	Sakaguchi *et al.* (1977)
Paramecium	LC50	7	9	Shaw (1954)
Polycelis nigra	LC50	7	16	Jones (1939b)
Daphnia magna	48h-LC50	5	23	Khangarot & Ray (1989)
Daphnia magna	48h LC50	5	9	Kimball (undated MS)
Daphnia magna	28d LC50	1	9	Kimball (undated MS)
Daphnia magna	28d-reproduction	1	9	Kimball (undated MS)
Daphnia magna	64h-EC50	8	19	Anderson (1948)
Daphnia magna	48h-EC50	6	15	Biesinger and Christensen (1972)
Daphnia hyalina	48h-EC50	7	12	Badouin and Scoppa (1974)
Cyclops abyssorum prealpins	48h EC50	8	12	Badouin and Scoppa (1974)
Tubifex tubifex	96h-EC50	24	32	Khangarot (1991)
Cypris subglobosa	48h-EC50	11	28	Khangarot and Ray (unpublished)
Lebistes reticulatus	LD50	8	9	Shaw and Grushkin (1957)
Gasterosteus aculeatus	LC50	11	18	Jones (1939a)
Pimephales promelas	192h-LC50	4	8	Kimball (undated MS)
Pimephales promelas	28d-survival	4	7	Kimball (undated MS)
Gastrophryne carolinensis	7d-LC50	11	22	Birge (1978)
Rana hexadactyla	96h-LC50	7	9	Khangarot *et al.* (1982)
Bufo valliceps	LD50	7	9	Shaw and Grushkin (1957)

2.4 EFFECTS OF WATER QUALITY PARAMETERS ON TOXICITY

Diamond *et al.* (1992) reported that water hardness had a significant effect on the toxicity of cobalt. Their studies showed that in the hardness range of 50 to 200 mg/L as $CaCO_3$, acute cobalt toxicity to both fish and invertebrates may be inversely

related to hardness. Toxicity of cobalt to fathead minnows appeared to increase at the highest hardness tested, however the authors state that toxicity may have been a result of the extreme hardness rather than cobalt toxicity. Diamond *et al.* (1992) suggested that it is possible that Ca^{2+} and Mg^{2+} compete with cobalt for potential target sites of toxic actions. Cobalt has a higher density and higher ionization potential than these ions and thus cobalt adsorption on cell membranes may not be a stable phenomenon given an abundance of more reactive cations available. This paper only reported NOECs for fathead minnow, instead of effect concentrations. As such, it is difficult to assess the true effects of hardness due to the possibility that toxic effects may not occur in proportion to the respective NOECs. Buikema *et al.* (1984) was the only other study that investigated hardness effects on cobalt toxicity. They reported that hardness had little effect on cobalt toxicity to rotifers over 96 hours.

3.0 BIOACCUMULATION

Cobalt may bioaccumulate in freshwater plants and invertebrates but does not accumulate in fish tissues. Although freshwater algae can have cobalt concentrations of 400 to $2x10^6$ times the ambient levels, it is uncertain to whether this is due to actual biological uptake or to physical adsorption (Cole and Carson 1981). Bioconcentration factors range from 100-14 000 for freshwater molluscs; up to 10^6 for insect larvae; and from 1-11 000 for other invertebrates (Cole and Carson 1981). Various species of fish sampled had cobalt concentrations ranging from 0.23 µg/g (fresh weight) to 4.7 µg/g in Lake Erie; 0.16 µg/g to 1.1 µg/g in Lake Ontario; and 0.04 µg/g to 0.33 µg/g in the St. Lawrence (Tong *et al.* 1972). The cobalt concentrations in lake trout (*Salvelinus namaycush*) which averaged 0.0599 µg/g (fresh weight), were found not to vary significantly with fish up to 12 years (Tong *et al.* 1974), suggesting that it does not biomagnify. ASTDR (1991) reports that benthic bottom feeding fish do not appear to significantly bioaccumulate cobalt from contaminated sediment.

Baudin and Fritsch (1989) examined the related contribution of food and water in the accumulation of cobalt in fish. Carp fed Co^{60}-contaminated snails were found to accumulate Co only slightly. The authors report a trophic transfer rate (transfer of contaminant residues from lower to higher trophic levels) of about 10^{-2}. Furthermore, the fish were found to depurate cobalt, resulting in a retention factor of only 3×10^{-3} after 63 days. Fish exposed to waterborne cobalt had uptakes significantly higher than those exposed through food, while fish exposed through both water and food had the highest uptake. The authors concluded that water is the primary route of cobalt uptake in carp and that accumulation from both food and water was additive.

4.0 IMPACT ON TASTE AND ODOUR OF WATER AND FISH TAINTING

In water, cobaltous bromide has a slight odour and cobaltous chloride has a slight sharp odour; cobaltous nitrate and sulfate are odourless (Weiss 1986). Concentrations at which these odours were detectable were not given. Organoleptic data were not available for tainting of fish flesh.

5.0 MUTAGENICITY

A review of summary documents was undertaken to examine the likelihood of cobalt causing mutagenic effects (ASTDR 1991, Smith and Carson 1981, IRIS 1994). A recent special issue of the journal, "The Science of the Total Environment" (Volume 150, 1994) contained a number of papers on the toxicity, mutagenicity and environmental fate of cobalt.

ASTDR (1991) reported that no studies were found describing genotoxic effects on humans or animals through inhalation, oral or dermal exposure to cobalt. It was reported that cobalt (II) was found to be generally non-mutagenic in bacteria and yeast, while cobalt (III) garnered positive mutagenic responses in *Salmonella typhimurium* and *Escherichia coli*. Further information suggested that cobalt was

genotoxic in *in vitro* experiments, causing genetic conversions in *S. cerevisae*, clastogenic effects on mammalian cells, transformations in hamster cells and sister chromatid exchanges in human lymphocytes. Sharma and Talukder (1987) report that cobalt exerts very strong mutagenic effects on plant activity. When compared to other inorganics, cobalt was found to be less toxic than arsenic and selenium, yet more toxic than lead, zinc or cadmium based on clastogenic tests with onion root tips (*Allium sp.*). Effects reported include chromosome breaks, diplochromatids, erosion, fragmentation and bridges. Cobalt salts reduced the rate of cell division, inhibited passage of interphase into prophase and produced clumping and stickiness of chromosomes in *Vicia sp.*

Nordberg (1994) reported that there was sufficient evidence of carcinogenicity for cobalt (II) oxide, limited evidence of carcinogenicity for cobalt (II) sulphide and cobalt (II) chloride, and inadequate evidence of carcinogenicity for cobalt aluminum spinel, cobalt (II, III) oxide, cobalt naphtenate and cobalt (III) acetate in animals.

ASTDR (1991) reported that cobalt has not been shown to cause cancer in humans by any exposure route. However, IARC (International Agency for Research on Cancer) recently classified cobalt and cobalt compounds as possible human carcinogens (Group B). This classification was based on limited evidence in humans, and data from studies that concluded that soluble cobalt (II) compounds are genotoxic to various organisms (Binderup and Wassermann 1994).

There is evidence that suggests that cobalt is teratogenic in mammalian systems (ASTDR 1991). There is some indication that cobalt may cause terata in aquatic invertebrates. Jaroensastraraks and McLaughlin (1974 as cited in Herndon *et al.*) reported that eggs of the freshwater snail, *Helisoma*, treated with 1 mg/L of cobalt had deformities of the shell and gut. Another study (Morrill 1963, in Herndon *et al.* 1981) reported that concentrations as low as 0.16 µg/L caused abnormalities in the shell and feet of gastropods. This study could not be critically reviewed for this document, and

was not used in objective derivation. Data by Sunderman (1992) suggested that low concentrations of cobalt (30 mg/L) may cause abnormalities in *Xenopus*, however this paper could not be obtained.

In summary, available information suggests that cobalt may exert genotoxic effects, with cobalt (III) likely exhibiting the most significant mutagenic effects. Recent evidence suggests that cobalt may cause cancer, and may result in terata in some organisms, including aquatic invertebrates.

6.0 DERIVATION OF THE PROVINCIAL WATER QUALITY OBJECTIVE

6.1 TOXICOLOGICAL DATA

For a PWQO to be developed, certain information requirements must be met (OMOE 1992a). These are summarized in Table 3. All requirements for developing a PWQO could be met with the existing data, except for a mutagenicity assessment. While cobalt has been shown to be mutagenic in lab animals, no primary data was available for aquatic organisms. Until sufficient mutagenicity information becomes available, a PWQO based solely on aquatic toxicity will be developed. It should be noted that this value may not protect against mutagenic effects.

While there is evidence suggesting that cobalt toxicity is affected by water hardness, there is insufficient toxicity data to allow development of a hardness-based PWQO. Thus, the most conservative approach will be taken and the PWQO will be set as a single value.

The lowest effect concentration of cobalt was 0.009 mg/L; based on a 28d LOEC (reproduction) for *D. magna* (Kimball undated MS). The initial safety factor of 10 (OMOE 1992a) was applied to this value to derive a preliminary PWQO of 0.0009 mg/L (0.9 µg/L) for the protection of aquatic life.

6.2 BIOACCUMULATION

Cobalt does not appear to bioaccumulate in fish. Thus, for the purposes of criterion development, bioaccumulation of cobalt was not considered significant. Therefore bioaccumulation will not affect the preliminary PWQO calculated from toxicity data.

6.3 MUTAGENICITY

There were few studies available which examined mutagenic effects on aquatic organisms. However, these data were from secondary literature sources and could not be properly reviewed. Data for mammalian systems indicates that cobalt may exert genotoxic effects, with cobalt (III) likely exhibiting the most significant mutagenic effects. Recent evidence suggests that cobalt may cause cancer, and may result in terata in some organisms. Therefore, the PWQO based on aquatic toxicity may not protect against these effects.

6.4 TASTE AND ODOUR

There was no information in the literature that indicates that cobalt would affect the taste and odour of water. In fact there is evidence to the contrary, it is tasteless and odourless.

6.5 OTHER EFFECTS

There is no evidence to suggest that the PWQO should be lowered to protect piscivorous wildlife.

6.6 DERMAL EFFECTS

The scant data available regarding dermal absorption of cobalt suggest that there should be no detrimental effects on humans exposed to environmental concentrations of cobalt while engaging in water based recreational activities (e.g. swimming).

ASTDR (1991) reported that no studies were found regarding lethal or significant non-lethal effects on humans after dermal exposure to cobalt, nor were any studies investigating rates of dermal absorption in humans found. Christie *et al.* (1976 in Herndon *et al.* 1981) found that cobalt poorly penetrated normal skin but may penetrate damaged skin more quickly. Herndon *et al.* (1981) reported that intermittent dermal exposure to a 0.5 to 2.5% $Co(NO_3)_2$ solution over periods ranging from 1 week to 35 years resulted in dermatitis and eczema. There have been reports of some people with severe dermal hypersensitivity to cobalt. Concentrations as low as 0.27% cobalt chloride in distilled water have elicited an effect.

6.7 OMOEE LABORATORY DETECTION LIMITS

Boomer (pers. comm.) reported that the routine OMOEE laboratory detection limit for cobalt in surface water is currently about 0.5 µg/L using pre-concentrated samples and ICP/MS technology. This value is lower than the proposed PWQO of 0.9 µg/L. However, there are problems when using this technique with samples containing high concentrations of iron, which may result in laboratory detection limits 2 to 3 orders of magnitude higher. Hence, in some instances, the PWQO may be below the detection limit.

6.8 CONCLUSION

In summary, the recommended PWQO for total cobalt is 0.0009 mg/L based on aquatic toxicity

7.0 RESEARCH NEEDS

Primary chronic and acute toxicity tests with vertebrates, especially coldwater North American species are required to provide a more comprehensive data base. Although there is fairly good breadth in the variety of species tested, there is very little depth in terms of several tests on important species. In general, experimental procedure in the future should include:

1. reporting the effect concentration in terms of mg metal ion/L instead of leaving it ambiguous and incomparable with other data. This is especially important for cobalt which has significant differences in molecular weight for hydrated and anhydrous salts, making conversions from mg/L salt to mg/L metal ion impossible if the specific form of salt used is not indicated.

2. studies on the toxic species and effects of water quality variables such as pH and hardness.

3. since there is evidence suggesting cobalt may have mutagenic properties, further investigations of these properties on aquatic organisms are needed.

4. since the data from Kimball (undated) was never published, similar experiments should be performed to assess the validity of the data.

5. The paper by Solski and Piontek (1987) reporting toxicity to *Dugesia* at very low concentrations of cobalt should be obtained and assessed.

6. The two papers examining the mutagenicity of cobalt (Morrill 1963, Sunderman 1992) should be obtained and assessed.

8.0 OBJECTIVES OF OTHER AGENCIES

There is no national Canadian cobalt guideline for the protection of freshwater aquatic life (CCREM 1987). There are however guidelines for livestock watering and irrigation water of 1.0 mg/L and 0.05 mg/L, respectively, for total cobalt (CCREM 1987). The U.S. EPA (1987) has a permissible ambient goal of 0.7 mg/L based on human health effects (Sittig 1985). A limit of 1.0 mg/L for cobalt in drinking water has been set in the U.S.S.R. (Sittig 1985). The New York State ambient water quality standard for cobalt of 5 µg/L in surface water is based on chronic reproductive toxicity to aquatic life (NYSDEC 1986).

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Table 2. Aquatic Toxicity Table for Cobalt

Common Name	Species Name	Life Stage	(1) Response	pH	Temp. (°C)	DO (mg/L)	Alk (mg/L)	Hard (mg/L)	Effect Conc (mg/L)	(2) Code	Reference	(3) Data Class
VERTEBRATES – ACUTE DATA												
Giant gourami	*Colisa fasciatus*	adult female	96h-LC50	7 3	25	6 4	–	120	56	SU	Srivastava & Agrawal 1979	SA
Fathead minnow	*Pimephales promelas*		96h-LC50	7 4	20	–	93	130	22	SU	Ewell et al 1986	SA
Fathead minnow	*Pimephales promelas*	5–15d	48h-NOEC	–	25	–	174 3	256 3	7 28	RM	Diamond et al 1992	PA
Fathead minnow	*Pimephales promelas*	8wk 12–16mm	96h-LC50	8 16	25 4	7 02	235	–	3 61	FM	Kimball MS	PA
Fathead minnow	*Pimephales promelas*	5–15d	48h-NOEC	–	25	–	10 7	57 2	1 245	RM	Diamond et al 1992	PA
Fathead minnow	*Pimephales promelas*	5–15d	48h-NOEC	–	25	–	576 8	882 4	6 2	RM	Diamond et al 1992	PA
Fathead minnow	*Pimephales promelas*		96h-LC50	7 2–7 9	22	–	33	44	32 2	SM	Curtis & Ward, 1981	SA
Fathead minnow	*Pimephales promelas*	5–15d	48h-NOEC	–	25	–	342 7	476 7	13 733	RM	Diamond et al 1992	PA
Fathead minnow	*Pimephales promelas*		96h-LC50	7 2–7 9	22	–	33	44	91 9	SM	Curtis & Ward, 1981	SA
Clawed frog	*Xenopus laevis*	embryo	96h-EC50 (abnormalities)	6 8	23	–	–	–	0 325	??	Sunderman 1992 (in AQUIRE)	SA
Clawed frog	*Xenopus laevis*	embryo	96h-LC50	6 8	23	–	–	–	13504	??	Sunderman 1992 (in AQUIRE)	SA
Clawed frog	*Xenopus laevis*	embryo	96h-LOEC (growth)	6 8	23	–	–	–	5 453	??	Sunderman 1992 (in AQUIRE)	SA
INVERTEBRATES – ACUTE DATA												
Crayfish	*Austropotamobius pallipes p*	19–32 mm	96h-LC50	7	16	Sat	–	–	8 8	RM	Boutet & Chaisemartin, 1973	PA
Amphipod	*Crangonyx pseudogracilis*	4 mm	48h-LC50	6.75	13	9 6	50	50	167	RU	Martin & Holdich, 1986	SA
Copepod	*Cyclops abyssorum*	adult, 0.62mm	48h-LC50	7 2	10	–	29	33	15 5	AU	Baudouin & Scoppa, 1974	SA
Daphnids	*Daphnia hyalina*	adult, 1 27mm	48h-LC50	7.2	10	–	29	33	1 32	SU	Baudouin & Scoppa, 1974	SA
Daphnids	*Daphnia magna*	<24h	48h-LC50	–	20	–	342 7	476 7	4 196	RM	Diamond et al 1992	PA
Daphnids	*Daphnia magna*	<24h	48h-LC50	–	20	–	174 3	256 3	4 595	RM	Diamond et al 1992	PA
Daphnids	*Daphnia magna*	<24h	48h-LC50 (unfed)	7 4–8.2		>9	42 3	45 3	1 11	RU	Biesinger & Christensen, 1972	SA
Daphnids	*Daphnia magna*	various	24h-LC50	7 6	13	5 6	400	240	2.11	SU	Khangarot et al , 1987	SA
Daphnids	*Daphnia magna*	various	48h-LC50	7 6	13	5 6	400	240	1 49	SU	Khangarot & Ray, 1989	SA
Daphnids	*Daphnia magna*	<8h	64h toxicity threshold	–	25	–	–	–	<1 41	SU	Anderson, 1948	A*
Daphnids	*Daphnia magna*	<24h	48h-LC50	–	20	–	576 8	882 4	>5 275	RM	Diamond et al 1992	PA
Daphnids	*Daphnia magna*	<24h	48h-LC50	–	20	–	10 7	57.2	2 347	RM	Diamond et al 1992	PA
Daphnids	*Daphnia magna*	<24h	48h-EC50 (fed)	8 16	25 4	7 02	235	–	7 37	SM	Kimball MS	PA
Daphnids	*Daphnia magna*	various	24h-LC50	7 8	13	5 6	400	240	2 61	SU	Khangarot & Ray 1989	SA

Table 2. Aquatic Toxicity Table for Cobalt

Common Name	Species Name	Life Stage	(1) Response	pH	Temp (°C)	DO (mg/L)	Alk (mg/L)	Hard (mg/L)	Effect Conc (mg/L)	(2) Code	Reference	(3) Data Class
Daphnids	*Daphnia magna*	<24h	48h-EC50 (unfed)	8 16	25 4	7 02	235	–	5 99	SM	Kimball MS	PA
Daphnids	*Daphnia magna*	<24h	48h-LC50 (fed)	7 4-8.2		>9	42 3	45 3	1 62	RU	Biesinger & Christensen, 1972	SA
Daphnids	*Daphnia magna*	various	48h-LC50	7 6	13	5 6	400	240	1 52	SU	Khangarot et al , 1987	SA
Insect	*Eudiaptomus padamus*	adult, 0.43mm	48h-LC50	7 2	10	–	29	33	4	SU	Baudouin & Scoppa, 1974	SA
Snail	*Helisoma tribolus*	0 180g	96h-LC50	7 4	20	–	93	130	>50	SU	Ewell et al , 1986	SA
Worm	*Lumbriculus variegatus*	0 006g	96h-LC50	7.4	20	–	93	130	>50	SU	Ewell et al , 1986	SA
Crayfish	*Orconectes limosus*	19-32 mm	96h-LC50	7	16	Sat	–	–	10 2	RM	Boutet & Chaisemartin, 1973	PA
Rotifer	*Philodina acuticornus*		24h-EC50	7.4-7.9	20	–	24	25	27 8	SU	Buikema et al., 1974	SA
Planarian	*Polycelis nigra*		48h-lethality threshold	5.8	15-18	–	–	–	83	RU	Jones, 1939	SA
Worm	*Tubifex tubifex*	adults	48h-EC50	7 6	30	5 8	400	245	447 71	SU	Khangarot 1991	SA
Worm	*Tubifex tubifex*	adults	24h-EC50	7 6	30	5 8	400	245	447 71	SU	Khangarot 1991	SA
VERTEBRATES - CHRONIC DATA												
Goldfish	*Carassius auratus*	embryo-larval	7d-LC50	7 4	22	sat	–	195	0 81	RM	Birge, 1978	PC
Stickleback	*Gasterosteus aculeatus*	3 5 cm	10d-NOEC	–	–	–	–	–	10	RU	Jones, 1939	SC
Narrowmouth toad	*Microhyla carolinensis*	embryo-larval	7d-LC50	7 4	22	sat	–	195	0 05	RM	Birge, 1978	PC
Rainbow trout	*Oncorhynchus mykiss*	embryo-larval	28d-LC50	7 4	13	sat	–	104	0.47	RM	Birge, 1978	PC
Fathead minnow	*Pimephales promelas*	8wk, 12-16mm	8d-LC50	8 16	25 4	7 02	235	–	2 74	FM	Kimball MS	PC
Fathead minnow	*Pimephales promelas*	embryo-larval	28d-posthatch (weight)	8 16	25 4	7 02	235	–	0.81	FM	Kimball MS	PC
Fathead minnow	*Pimephales promelas*	5-15d	7d-surv /growth	–	25	–	10 7	57.2	1 232	RM	Diamond et al 1992	PC
Fathead minnow	*Pimephales promelas*	embryo-larval	28d-posthatch (MATC)	8 16	25 4	7 02	235	–	0.29	FM	Kimball MS	PC
Fathead minnow	*Pimephales promelas*	5-15d	7d-surv /growth	–	25	–	576 8	882.4	3 833	RM	Diamond et al 1992	PC
Fathead minnow	*Pimephales promelas*	5-15d	7d-surv /growth	–	25	–	174 3	256 3	1 794	RM	Diamond et al 1992	PC
Fathead minnow	*Pimephales promelas*	5-15d	7d-surv /growth	–	25	–	342 7	478 7	1 932	RM	Diamond et al 1992	PC

Table 2. Aquatic Toxicity Table for Cobalt

Common Name	Species Name	Life Stage	(1) Response	pH	Temp (°C)	DO (mg/L)	Alk (mg/L)	Hard (mg/L)	Effect Conc (mg/L)	(2) Code	Reference	(3) Data Class
Fathead minnow	*Pimephales promelas*	embryo-larval	28d-posthatch (survival)	8.16	25.4	7.02	235	–	1.61	FM	Kimball MS	PC
Tilapia	*Sarotheradon mossambicus*	10-12g	15d decrease in haemoglobin/ increase in haematocrit	–	28	–	–	–	15	SU	Pamila et al. 1991	SC
INVERTEBRATES – CHRONIC DATA												
Stonefly	*Acroneuria lycorias*		8d-LC50	7.2	18.5	8	66	50	32	SM	Warwick & Bell, 1969	SC
Crayfish	*Austropotamobius pallipes p*	19-32 mm	30d-LC50 (unfed)	7	16	Sat	–	–	0.79	RM	Boutet & Chaisemartin 1973	PC
Crayfish	*Austropotamobius pallipes p*	19-32 mm	30d-LC50 (fed)	7	16	Sat	–	–	0.77	RM	Boutet & Chaisemartin, 1973	PC
Amphipod	*Crangonyx pseudogracilis*	4 mm	96h-LC50	6.75	13	9.6	50	50	39.2	RU	Martin & Holdich, 1988	SC
Daphnids	*Daphnia magna*	<24h	3wk 18% reprod. impair	7.4-8.2		>9	42.3	45.3	0.01	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	3wk 12% protein increase	7.4-8.2		>9	42.3	45.3	0.024	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	7d-surv./reprod	–	20	–	174.3	256.3	<0.05	RM	Diamond et al. 1992	PC
Daphnids	*Daphnia magna*	<24h	7d-survival/reprod.	8.16	25.4	7.02	235	–	0.02	SM	Kimball MS	PC
Daphnids	*Daphnia magna*	<24h	96h-LC50	7.4	20	–	93	130	1.5	SU	Ewell et al., 1986	SC
Daphnids	*Daphnia magna*	<24h	28d-MATC	8.18	25.4	7.02	235	–	0.051	SM	Kimball MS	PC
Daphnids	*Daphnia magna*	<24h	3wk 12% wt. decrease	7.4-8.2		>9	42.3	45.3	0.024	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	7d-surv./reprod	–	20	–	578.8	882.4	0.6	RM	Diamond et al. 1992	PC
Daphnids	*Daphnia magna*	<24h	3wk 15% wt. decrease	7.4-8.2		>9	42.3	45.3	0.024	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	28d-survival/reprod	8.16	25.4	7.02	235	–	0.009	SM	Kimball MS	PC
Daphnids	*Daphnia magna*	<24h	28d-LC50	8.16	25.4	7.02	235	–	0.027	SM	Kimball MS	PC
Daphnids	*Daphnia magna*	<24h	96h-EC50 (fed)	8.16	25.4	7.02	235	–	1.86	SM	Kimball MS	PC
Daphnids	*Daphnia magna*	<24h	3wk LC50	7.4-8.2		>9	42.3	45.3	0.021	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	3wk 50% reprod. impair	7.4-8.2		>9	42.3	45.3	0.012	RU	Biesinger & Christensen, 1972	SC
Daphnids	*Daphnia magna*	<24h	7d-surv./reprod	–	20	–	342.7	476.7	0.05	RM	Diamond et al. 1992	PC
Daphnids	*Daphnia magna*	<24h	7d-surv./reprod	–	20	–	10.7	57.2	<0.05	RM	Diamond et al. 1992	PC
Planarian	*Dugesia tigrina*	11-12mm, 18-24d	10d-LC50	–	20	–	–	–	0.707	??	Solski & Piontek 1987 (in AQUIRE)	SC
Planarian	*Dugesia tigrina*	11-12mm, 18-24d	10d-Regeneration time?	–	20	–	–	–	0.002	??	Solski & Piontek 1987 (in AQUIRE)	SC
Planarian	*Dugesia tigrina*	0.006g	96h-LC50	7.4	20	–	93	130	11	SU	Ewell et al., 1986	SC
Mayfly	*Ephemerella ignita*	nymph	4wk growth inhib	5.6-6.5	3-19.3	–	–	–	0.03	FM	Sodergren, 1976	SC

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Common Name	Species Name	Life Stage	(1) Response	pH	Temp. (°C)	DO (mg/L)	Alk (mg/L)	Hard (mg/L)	Effect Conc. (mg/L)	(2) Code	Reference	(3) Data Class
Mayfly	*Ephemerella mucronata*	nymph	96h-LC50	-	2.5-14	-	-	-	33	SU	Sodergren, 1976	SC
Mayfly	*Ephemerella subvaria*		96h-LC50	6.9	18.5	8	46	50	16	SM	Warwick & Bell, 1969	SC
Sideswimmer	*Gammarus fasciatus*	0.007g	96h-LC50	7.4	20	-	93	130	>50	SU	Ewell et al., 1986	SC
Snail	*Halisoma sp.*	egg to embryo	dev. of terata						1	??	Jaroensastraraks & McLaughlin (1974)	SC
Snail	*Helisoma sp*	egg to embryo	dev. of terata						100	??	Jaroensastraraks & McLaughlin (1974)	SC
Caddisfly	*Hydropsycho betteni*		96h-LC50	7	18.5	8	46	46	64	SM	Warwich & Bell, 1969	SC
Snail	*Lymnaea palustris*	egg to embryo	dev. of terata						0.00016	??	Morril 1963 (in Herndon et al. 1981)	SC
Snail	*Lymnaea palustris*	egg to embryo	dev. of terata						0.0081	??	Morril 1963 (in Herndon et al. 1981)	SC
Crayfish	*Orconectes limosus*	19-32 mm	30d-LC50 (fed)	7	16	Sat	-	-	0.79	RM	Boutet & Chaisemartin, 1973	PC
Crayfish	*Orconectes limosus*	19-32 mm	30d-LC50 (unfed)	7	16	Sat	-	-	0.88	RM	Boutet & Chaisemartin, 1973	PC
Worm	*Tubifex tubifex*	adults	96h-EC50	7.6	30	5.8	400	245	139.32	SU	Khangarot 1991	SC
Worm	*Tubifex tubifex*	adults	inhib. nuclear expansion	6.7	-	c stress	-	-	10	SU	Fischer et al., 1980	SC
PLANTS, ALGAE and BACTERIA - CHRONIC DATA												
Algae	*Anabaena variabilis*		120h-EC50 (dry weight)	-	21	-	-	-	14.4	SU	Sharma et al., 1987	SC
Algae	*Anabaena variabilis*		144h-EC50 (dry weight)	-	21	-	-	-	10.9	SU	Sharma et al., 1987	SC
Algae	*Anabaena variabilis*		168h-EC50 (dry weight)	-	21	-	-	-	8.13	SU	Sharma et al., 1987	SC
Algae	*Anabaena variabilis*		96h-EC50 (dry weight)	-	21	-	-	-	23.8	SU	Sharma et al., 1987	SC
Algae	*Anabaena variabilis*		96h-no growth	-	26	-	-	-	50	SU	Ahluwalia & Kaur, 1988	SC
Algae	*Anabaena variabilis*		96h-decreased growth	-	26	-	-	-	20-50	SU	Ahluwalia & Kaur, 1988	SC
Algae	*Anacystis nidulans*		12d sign. growth inhibition	7.9	-	-	-	-	10	SU	Lee et al. 1992	SC
Algae	*Anacystis nidulans*		12d 100% growth inhibition	7.9	-	-	-	-	15	SU	Lee et al. 1992	SC

Table 2 Aquatic Toxicity Table for Cobalt

Common Name	Species Name	Life Stage	(1) Response	pH	Temp (°C)	DO (mg/L)	Alk (mg/L)	Hard (mg/L)	Effect Conc (mg/L)	(2) Code	Reference	(3) Data Class
Protist	*Chilomonas sp*		3h-HTC	7.6	26	-	-	-	1000	SU	Ruthven & Cairns, 1973	SC
Algae	*Chlamydomonas eugametos*		100% growth inhib	6.8	-	-	-	-	0.5	SM	Hutchinson, 1973	SC
Algae	*Chlorella vulgaris*		3-4mo growth inhib NOEC	7	20	-	-	-	0.226	SU	den Dooren de Jong, 1965	SC
Algae	*Chlorella vulgaris*		3-4mo growth inhib LOEC	7	20	-	-	-	0.442	SY	den Dooren de Jong, 1965	SC
Algae	*Chlorella vulgaris*		4-16d growth inhib	-	26	-	-	-	20-50	SU	Ahluwalia & Kaur 1988	SC
Algae	*Chlorella vulgaris*		99.7% growth inhib	6.8	-	-	-	-	1	SU	Hutchinson, 1973	SC
			21d-EC50	-	21	-	-	-	0.55	SM	Coleman et al., 1971	SC
Algae	*Haematococcus capensis*		80% growth inhib	6.8	-	-	-	-	5	SU	Hutchinson, 1973	SC
Protist	*Paranema sp.*		3h-HTC	7.6	26	-	-	-	2500	SU	Ruthven & Cairns, 1973	SC
Algae	*Scenedesmus acutiformis*		6-8d EC50	-	22	-	-	-	0.1	SM	Stokes, 1981	SC
Algae	*Scenedesmus acutiformis f. alternans*		6-8d EC50	-	22	-	-	-	0.25	SM	Stokes, 1981	SC
Algae	*Scenedesmus quadricauda*		20d 60.7% growth inhibition	8	30	8	-	-	5	SU	Hosetti et al. 1993	SC

Definitions

1. Response

LC - Lethal Concentration
EC - Effect Concentration
NOEC - No Effect Concentration
LOEC - Lowest Effect Concentration
red - Reduction
HTC - Highest Concentration where some organisms survive

2. Data Codes

F - Flowthrough
S - Static
R - Renewal
M - Measured
U - Unmeasured
A - Ancillary
? - Unknown (2° source)

3. Data Class

P - Primary
S - Secondary
A - Acute
C - Chronic
* - Ancillary

Table 3: Data Requirements for Provincial Water Quality Objectives

1. **Toxicity**

All data must be primary or chronic: marine or brackish species are not permitted.

FISH

At Least:

X	One coldwater species - *Rainbow trout* (Birge 1978)
X	One warmwater species - *Fathead minnow* (Diamond *et al.* 1992)
X	One other warmwater or coldwater species - *Toad* (Birge 1978)

With at least:

X	One species resident in Ontario (may be one of above) - *Rainbow trout* (Birge 1978)
X	One early lifestage endpoint - *9d-ELS for fathead minnows* (Diamond *et al.* 1992)
X	one other whole organisms chronic endpoint - *28d-LC50 for rainbow trout* (Birge 1978)

INVERTEBRATES

At Least:

X	one crustacean - *Daphnia magna* (Diamond *et al.* 1992)
X	One other order - *Crayfish* (Boutet & Chaisemartin 1973)

With at Least:

X	no more than one tropical species
X	one early lifestage endpoint - *7d-LOEC (reproduction of Daphnia as # of young per female)* (Diamond *et al.* 1992)
X	one other chronic endpoint - *30d-LC50 with crayfish* (Boutet & Chaisemartin 1973)

ALGAE/AQUATIC PLANT

X	one algae or aquatic plant resident in temperate North America using scientific procedures and test conditions compatible with recognized algal bioassays - *Green algae* (Coleman *et al.* 1971)

2. **Bioaccumulation**

One of:

	Fish consumption limit (e.g. Health and Welfare Guideline)
	an acceptable daily intake limit
	contaminant residue in aquatic biota value

and:

	A bioconcentration factor ≥ 1000 (In the absence of consumption limits, bioaccumulation may be significant and the Guideline setting process should be followed)

or:

X	A bioconcentration factor ≤ 1000 (In the absence of consumption information, bioaccumulation is not considered to be significant).

If BCF data is unavailable:

	Log Kow ≥ 4.00, then bioaccumulation is assumed to be significant and the Guideline setting process should be followed.

or:

	Log Kow ≤ 4.00, then bioaccumulation is assumed not to be significant.

3. Mutagenicity

A) For Initial Assessment

	Chemical is considered to be non-mutagenic (i.e. data from a minimum of two test systems, including tests for mutagenic as well as chromosomal damage endpoints, clearly demonstrating.

or:

?	Chemical is considered to be mutagenic in aquatic or mammalian systems. - *Possibly, data is inconclusive*

B) For Setting PWQOs (A total of three studies are required for mutagenicity.

VERTEBRATES

(All data must be primary and measured in whole aquatic organisms, Marine and brackish tests are not permitted)

Data from at least one of the following three categories:

	fish - mutagenicity related diseases
	fish - mutagenicity or chromosomal aberrations
	other vertebrate mutagenicity of chromosomal aberration

INVERTEBRATES

Data from a maximum of two of the following three categories:

	invertebrate - mutagenicity or chromosomal aberration
	aquatic plant - mutagenicity or chromosomal aberration
	microbial - mutagenicity

FIG. 1a: DERIVATION GRAPH - COBALT, ACUTE TOXICITY

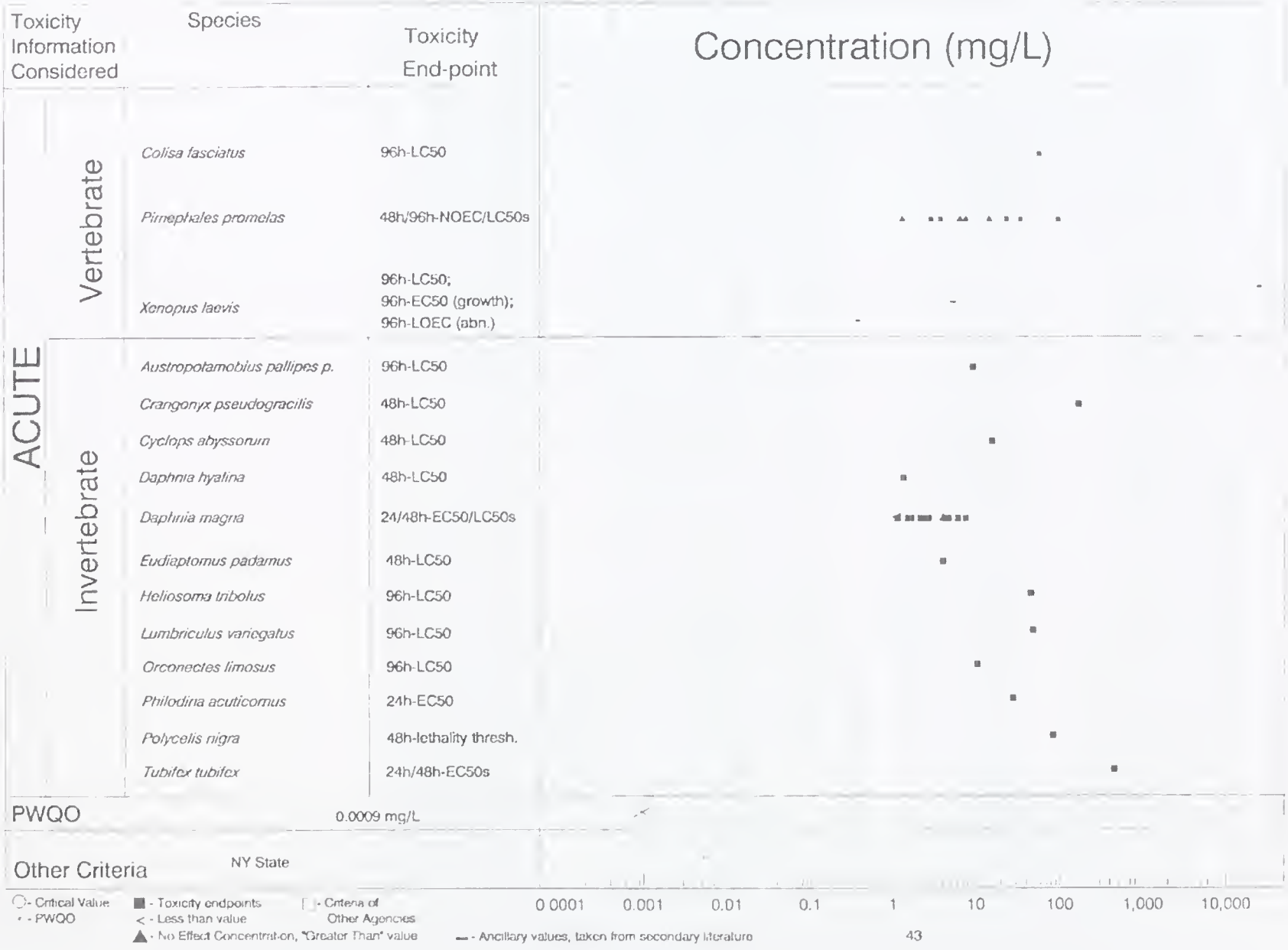

FIG. 1b: DERIVATION GRAPH - COBALT, CHRONIC TOXICITY